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Measurements of the  $O^+ + N_2$  and  $O^+ + O_2$  reaction rates from 300 to 900 K

Aikwo Chen, Rainer Johnsen and Manfred A. Biondi

Dept. of Physics and Astronomy

University of Pittsburgh

Pittsburgh, PA 15260

Abstract

Rate coefficients for the  $O^+ + N_2$  atom transfer and  $O^+ + O_2$  charge transfer reactions are determined at thermal energies between  $\sim 300$  K and  $\sim 900$  K in a heated drift tube - mass spectrometer apparatus. At 300 K the values  $k(O^+ + N_2) = (1.2 \pm 0.1) \times 10^{-12}$   $\text{cm}^3/\text{sec}$  and  $k(O^+ + O_2) = (2.1 \pm 0.2) \times 10^{-11}$   $\text{cm}^3/\text{sec}$  are obtained, with a  $\sim 50\%$  decrease in the reaction rates upon heating to 700 K. These results are in good agreement with heated flowing afterglow results, but the  $O^+ + O_2$  thermal rate coefficients are systematically lower than equivalent Maxwellian rates inferred by conversion of non-thermal drift tube and flow-drift data.

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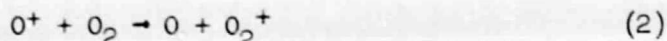


## Introduction

Primarily because of their importance in the F-region of the earth's ionosphere, the atom transfer reaction



and the charge transfer reaction



have been the subject of a number of laboratory investigations<sup>1-6</sup>. The variation with temperature of the rate coefficients may be determined in two different ways. One approach is to raise the  $\text{O}^+$  ions' kinetic energy by application of electric fields in a standard drift tube<sup>2</sup> (DT) or in a flow-drift tube<sup>4</sup> (FD). Reaction rates measured in this way are converted to equivalent Maxwellian rate coefficients by use of modern techniques to calculate the ions' velocity distribution under the action of the electric field<sup>7</sup>. While this procedure simulates an elevated ion translational temperature, the neutral molecules remain at the gas temperature (typically 300 K). A second method of obtaining the temperature variation of the rate coefficients employs actual heating of the apparatus and the gases contained therein<sup>3,5</sup>. In this case, the internal degrees of freedom (rotational and vibrational) of the reactant molecules are in equilibrium with the translational degrees of freedom, all at the elevated temperature of the gas.

As a result of the differences in internal energy of the molecules, the two experimental techniques may not yield the same "temperature" dependence for the rate coefficients. For example, at moderate temperatures (300 to 900 K) the behavior of the atom transfer rate coefficient is usually controlled by the formation of an intermediate, unstable reaction

complex,  $N_2O^+$ , in the case of reaction (1). Since the unimolecular decomposition rate of this complex usually depends strongly on the excess energy in the complex, changes in the internal energy of the  $N_2$  should affect the overall reaction rate.

Utilization of the heating technique has been hampered severely by experimental difficulties in constructing and operating an apparatus that can withstand the high temperatures involved. Temperatures of up to 900 K have been obtained in a heated flowing afterglow apparatus, and a number of reactions have been studied in that apparatus<sup>5</sup>. In the present investigation a high temperature drift tube was designed for a maximum temperature of  $\sim 1500$  K. While this temperature is readily attained without causing damage to the instrument, reliable measurements above 930 K have not been obtained because of several experimental problems. The present studies have yielded data for the  $O^+ + N_2$  reaction rate up to 930 K which exhibit substantially less scatter than the measurements obtained in the heated flowing afterglow apparatus<sup>3,5</sup>. Studies of the  $O^+ + O_2$  reaction with the present apparatus were limited to temperatures  $\leq 700$  K as a result of reaction between the oxygen gas and the tantalum walls of the drift tube.

#### Experimental apparatus

The apparatus consists of a small tantalum drift tube (drift length, 11.53 cm; diameter, 5 cm) contained in a large vacuum chamber (see Fig. 1). Electric heaters in contact with the outside of the drift tube are surrounded by multiple radiation shields to reduce heat losses. The temperature is measured by means of several platinum/platinum-rhodium thermocouples (attached to the drift tube walls and guard ring electrodes) and by an optical pyrometer which views the outside wall of the drift tube.

### Measurements

The studies of the  $O^+ + N_2$  and  $O^+ + O_2$  reactions were preceded by a series of measurements of the fast reactions  $He^+ + N_2$  and  $He^+ + O_2$  which are known to have nearly temperature-independent rate coefficients over a wide range. The primary purpose of these tests was to learn whether at high temperatures chemical interactions between the reactant gas and the walls of the drift tube would change the gas composition and thus lead to incorrect determinations of the rate coefficients. No such effects were observed for nitrogen reactant up to temperatures of 950 K. Measurements with oxygen reactant showed a substantial and unpredictable reduction of the oxygen density at temperatures above 700 K, apparently due to an oxidation reaction with the hot tantalum walls.

Although ordinary outgassing of the drift tube walls at high temperatures was not found to be a serious problem, alkali ions were observed above 750 K, probably arising from alkali impurities in the tantalum which were surface-ionized at the elevated temperatures. While these ions persisted throughout the course of the measurements, they apparently had no effect on the rate coefficient determinations.

It was found that at temperatures above 1000 K many ions were produced in the drift region, even when the ion source was not operating. Estimates indicated that, even though the thermionic emission of tantalum at 1000 K is quite small, enough electrons are emitted from the large surface areas in the tube to produce the observed ion currents. Attempts were made to reduce the ionization produced by these electrons by working at low electric fields, but no conditions suitable for accurate rate coefficient measurements could be obtained above 1000 K.

## Results

### a) $O^+ + N_2$

Rate coefficients for this reaction were derived from the observed loss of  $O^+$  ions at temperatures ranging from 320 to 930 K. No systematic variation of the rate coefficient with total gas pressure or with the  $N_2/Ar$  mixing ratio (0.18 to 0.36) was found, as should be the case for a two-body reaction. No deviation from a purely exponential decay of the  $O^+$  ions with additional residence time was observed. Such deviations can arise if the parent ions are present in different excited states that react at different rates. For example, the metastable  $O^+(^2D)$  ions are known<sup>9,10</sup> to react with  $N_2$  over 100 times faster than do  $O^+(^4S)$  ground state ions.

The results of the present experiment are shown in Fig. 2, together with the published data of Lindinger, et al<sup>5</sup> obtained in a heated flowing afterglow system and the flow-drift data of Albritton, et al<sup>6</sup> which have been converted to equivalent "thermal" rate coefficients by the procedure of Lin and Bardsley<sup>7</sup>. (We have not converted our earlier, non-thermal measurements<sup>2</sup> of  $O^+ + N_2$ , since the required calculation of the ion velocity distribution in a gas mixture containing an appreciable fraction of  $N_2$  molecules is not presently available.) The agreement between the three sets of data at 300 K is quite good. At higher temperatures the present data lie systematically below the heated afterglow results, although within the large scatter of those data. The difference between the present results and the flow-drift tube data (converted to equivalent "thermal" rate coefficients) is small.

b)  $O^+ + O_2$ 

The experimental procedures used in the determination of this rate coefficient were identical to those in the  $O^+ + N_2$  work. Total pressures ranging from 0.27 to 1.0 Torr and  $O_2/Ar$  mixing ratios from 0.012 to 0.032 were employed. It was found that at temperatures above  $\sim 700$  K reliable rate coefficients could not be obtained, because the oxygen began to react with the tantalum walls of the drift tube. Attempts were made to determine the resulting reduction in the  $O_2$  density by admitting pure  $O_2$  to the drift tube at a constant rate and monitoring the pressure change as a function of temperature. These tests indicated that at temperatures above 800 K the  $O_2$  density was only  $\sim 1\%$  of that measured at 700 K. Similar measurements carried out with argon and with nitrogen showed no such effects up to 900 K, i.e. the reduction in pressure depended strongly on the chemical reactivity of the gas used.

The rate coefficients were determined up to a maximum temperature of 715 K, as shown in Fig. 3. The agreement between the present data and those of Lindinger et al.<sup>5</sup> obtained in the heated flowing afterglow system is very good. The converted FD and DT drift data<sup>2,6</sup>, while in agreement with the heated drift-tube and flowing afterglow results at 300 K, yield systematically higher rate coefficients as the temperature is increased, the difference reaching  $\sim 30\%$  at 700 K.

Discussion and Conclusions

In the case of the  $O^+ + N_2$  reaction the present rate coefficients determined with the heated drift tube exhibit substantially reduced scatter and suggest a stronger decrease with increasing gas temperature than do the heated flowing afterglow results<sup>5</sup>. The agreement of the converted flow-drift tube results<sup>6</sup> (which correspond to elevation of the



ions' translational temperature) with our heated drift tube measurements suggests that, up to  $\sim 900$  K, thermal excitation of the vibrational and rotational degrees of freedom of the  $N_2$  molecule is not sufficient to measurably affect the reaction rate. Earlier flowing afterglow studies<sup>11</sup> involving low translational temperatures ( $\sim 300$  K) and high vibrational temperatures ( $T_v > 1000$  K) showed a striking increase in the  $O^+$  and  $N_2$  reaction rate when  $T_v$  was elevated sufficiently.

In the case of the  $O^+ + O_2$  reaction both the heated flowing afterglow and heated drift tube results are in good agreement and systematically lower than the converted ion-drift results<sup>2,6</sup> suggesting either that excitation of the internal degrees of freedom of the  $O_2$  molecule has a depressing effect on the reaction rate or else that the energy distribution function calculation required to convert the ion-drift data to an equivalent Maxwellian rate was inaccurate.

Unfortunately it has not been possible to extend the thermal studies to temperatures  $> 1000$  K where we had expected to observe a very rapid increase in the  $O^+ + N_2$  rate coefficient with increasing temperature. Since the effect of simultaneously increasing both ion translational and molecular vibrational energy can not be deduced from the earlier determinations of the separate effects, there is considerable uncertainty concerning the rate coefficient for  $O^+ + N_2$  in a thermal environment above  $T \sim 1000$  K, a condition often encountered in the F-region.

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Figure Captions

- Fig. 1 Schematic diagram of the differentially-pumped, heated drift tube and quadrupole mass spectrometer apparatus.
- Fig. 2 Measured rate coefficients as a function of temperature for the  $O^+ + N_2$  atom transfer reaction. The solid dots and curve represent the present results obtained with the heated drift tube, the crosses represent the heated flowing afterglow results of Lindinger, et al, and the dashed line represents the center-of-gravity ( $\pm 10\%$  accuracy) of the converted flow-drift data of Albritton, et al.
- Fig. 3 Measured rate coefficients as a function of temperature for the  $O^+ + O_2$  charge transfer reaction. Same symbols as in Fig. 2, except that the converted drift data also include the results of Johnsen and Biondi.

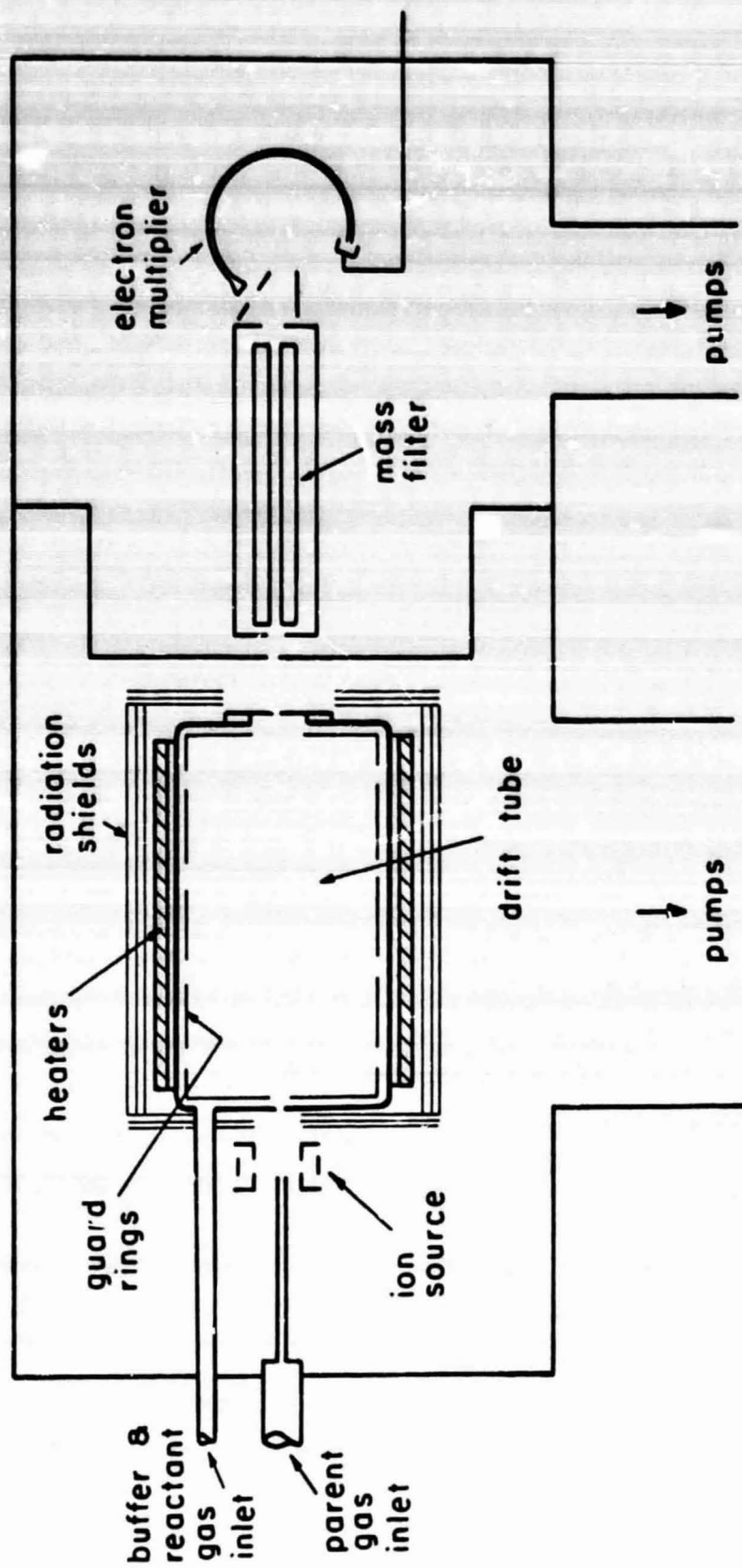


Fig. 1

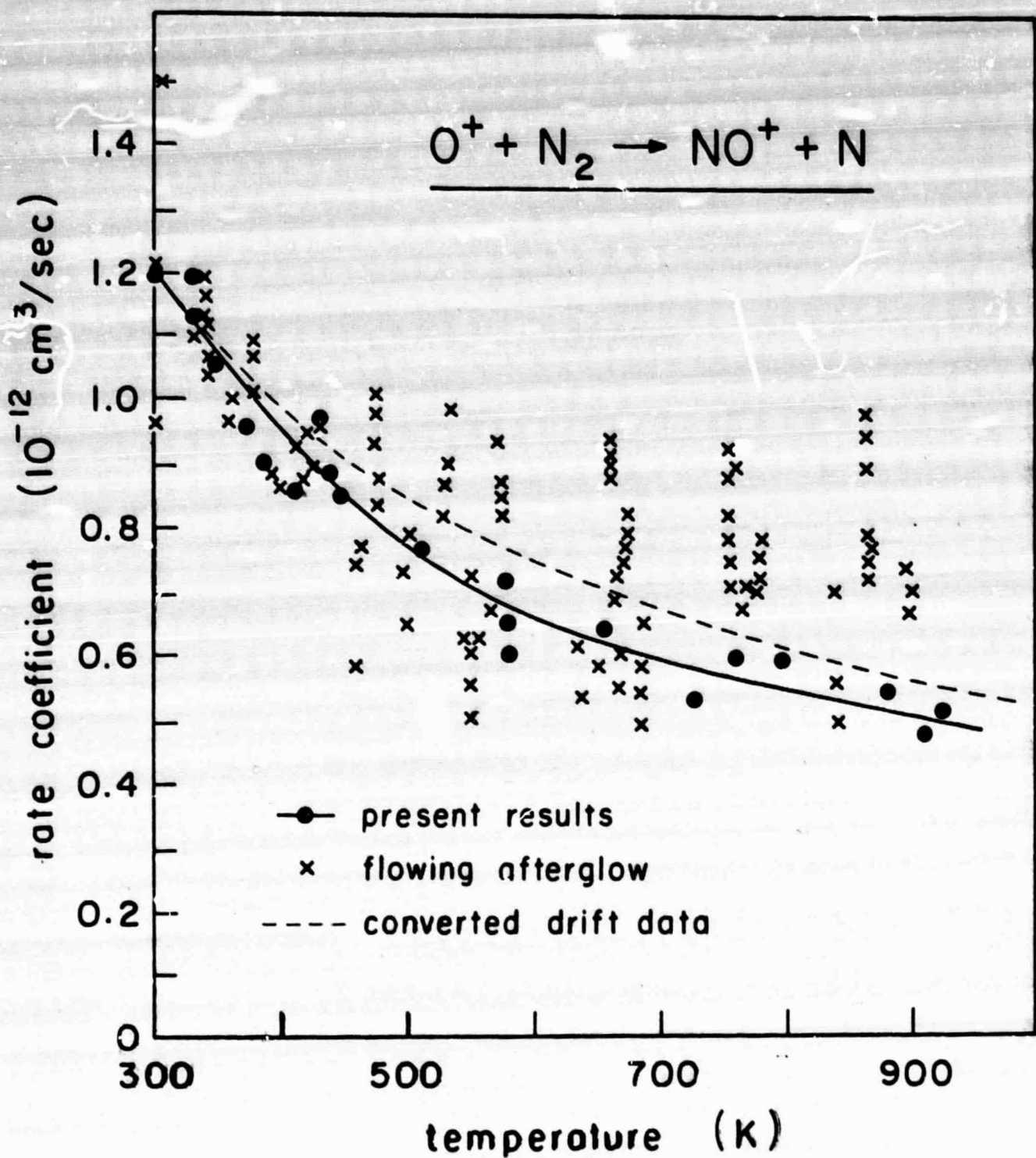


Fig. 2

